# DURABLE ANTIMICROBIAL LEATHER

## CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority based upon U.S. Provisional Application 60/398,922 filed July 26, 2002, entitled DURABLE ANTIMICROBIAL LEATHER THAT INHIBITS THE GROWTH OF BACTERIA, FUNGUS, MOLD AND MILDEW.

## FIELD OF THE INVENTION

[0002] The invention relates generally to processes for fabricating leather having antimicrobial properties, and more particularly to leather having antimicrobial properties where the antimicrobial properties are durable or an intrinsic part of leather.

## BACKGROUND OF THE INVENTION

[0003] Originally, leathers and skins were tanned with vegetable extracts and quite often with extracts from trees such as the oak and chestnut. These tanning agents were known for having antiseptic properties.

[0004] Typically, leathers were tanned with an excess of these tanning agents. The leathers would take up a considerable quantity of these agents and later exude them when combined with perspiration or other sources of moisture. The antiseptic function of these agents within the leather was thus indirectly transmitted to the skin and reduced the colonization of bacteria, fungi and other microscopic organisms.

[0005] Natural vegetative tanning agents have largely been supplanted in more modern tanning processes. Mineral agents are now widely used in mass tanning processes due to their lower cost and their ability to produce leathers and hides having desirable and uniform properties. One drawback to using

mineral tanning agents appears to be an associated increase in the development of microbial colonization of leather goods. Such colonization reduces the useful life of the goods through damage to structural integrity (e.g., rot) and staining among other problems.

[0006] Human fungal infections (i.e., mycosis) and other skin diseases have been linked to fungal colonization of leather shoes. This problem is of particular concern to the military. As is somewhat intuitive, studies have shown that once a leather article, such as a shoe, becomes infected with microbes the leather becomes a natural vehicle for transmission of infection or re-infection. It should be noted, however, that such infections are not limited to mineral tanned leathers but have also occurred where vegetative tanning agents have been used.

[0007] Accordingly, researchers have long sought methods for preventing microbial colonization of leather goods and the occurrence and transmission of microbial infections via leather goods.

[0008] The first efforts in this regard primarily employed the topical application of antimicrobial agents to leather hides either before the tanning process or after the tanning process. In very general terms, as leather is manufactured, it goes through three stages. In the first stage the hide is treated to remove hair. The second stage is the wet manufacturing stage where the hides are cleaned, scoured, dyed and usually waterproofed. The last stage is dry finishing in which the leather is stretched to almost double its size, the leather is split in half and various finishes are applied to the smooth surface for aesthetics.

[0009] Currently the majority of leather is treated with antimicrobial agents in the first stage and in the last stage. The wet hide is treated to prevent spoilage during shipping and storage, but the treatment is not durable and does not survive the tanning process to impart permanent antimicrobial properties to the finished leather. In the last stage the antimicrobial agents are spray applied to the outside surface of the leather and dried. This application

technique enables leather manufacturers to pass a stringent soil burial fungal test developed by the military, but the antimicrobial agents are not durable to washing or to other water contact. As the leather is used, and most notably exposed to rain and water, the antimicrobial agent washes away and the leather loses its antimicrobial properties.

**[0010]** Accordingly, what is needed is durable antimicrobial leather, which remains resistant to bacteria, fungi, mold and mildew long after the finishing process. The antimicrobial agents should be available throughout the leather, inside and on the surface to thoroughly protect the leather from stain and odor causing microbes, including bacteria and fungi.

## DESCRIPTION OF THE INVENTION

**[0011]** In broad terms the invention encompasses leather goods having durable antimicrobial properties because they possess antimicrobial agents. As used herein the term antimicrobial agent is used to encompass materials, typically chemicals that kill microbes or retard the growth of microbes to a commercially acceptable degree. The term antimicrobial agent should be understood to include bactericides and fungicides and other such agents. This detailed description uses the terms antimicrobial, bactericide and fungicide and those skilled in the art will be able to discern the appropriate meaning of each term by its context.

**[0012]** In a further embodiment, the invention encompasses a composition for treating leather during the wet portion of the tanning process. The composition can be exhausted into the leather to durably inhibit the growth of bacteria and fungus on the surface of the leather and in the interior of the leather. In general terms, the composition comprises a broad-spectrum bactericide, such as triclosan, in combination with a fungicide such as tolyldiiodomethylsulfone. The scientific name for triclosan is chloro-2-(2,4-dichlorophenoxy)phenol and it is commercially available from a number of

sources including the assignee of the present invention. Tolyldiiodomethylsulfone is also commercially available and one source is Angus Chemical which sells it under the trade names Amical® Flowable and Amical® 48.

**[0013]** A still further embodiment of the invention is a method for the aqueous treatment of leather goods to impart durable antimicrobial characteristics. As used herein the term aqueous means that the method according to the invention applies antimicrobial agents during the wet portion of the tanning process. Some references refer to this as "in-situ" application. In other words, the antimicrobial composition is applied during the soaking baths that are part of the tanning process. This type of application should be contrasted to the more common method of spray applying antimicrobial agents on the surface of the leather goods at the very beginning or at the end of the tanning process. The paragraphs that follow provide more detail regarding each embodiment of the invention using the method embodiment as a framework for the overall discussion.

**[0014]** As an initial matter, it should be understood that no two tanneries are identical; each has its unique characteristics and subprocesses. Some perform only some of the steps in the overall process and transfer the leather to other tanneries to complete the process. Accordingly, this detailed description contains a general overview of a typical process. Those skilled in the art are fully capable of taking the teachings of this invention and modifying them for application in any particular process. Detailed examples for a particular process are provided at the end of the discussion to further aid in the explanation of the invention.

**[0015]** In a typical process, the leather, as a blue hide, is first cleaned and scoured to remove fat using a solution of metal salts of various acids. Exemplary acids include acetic acid, carbonic acid, formic acid and sulfurous acid. This solution is often neutralized to a pH of about 7. The leather is then soaked and washed one or more times. Typically a wetting agent is added to the wash.

[0016] The leather goods are then soaked in an antimicrobial composition comprising a bactericide and a fungicide. Preferably the bactericide and fungicide composition is mixed with a lipophilic emulsifying agent such as the sodium salt of oleoylsarcosine in water. Sarcosine is a common name for N-methylamino acetic acid (aka N-methylglycine), a proteinaceous acid. This initial soaking can be the only soaking or it can be the first of several soakings For descriptive purposes this soaking will be referred to as the first soaking.

[0017] In preferred embodiments the antimicrobial composition comprises a fungicide and a bactericide in a ratio between about 1:50 and 10:1 fungicide to bactericide. In particularly preferred embodiments the fungicide is present in the antimicrobial composition between about 200 ppm and about 5,000 ppm, and the bactericide is present in the composition between about 500 ppm and between about 10,000 ppm based on the weight of the leather goods.

[0018] The bactericide may be selected from the group consisting of triclosan, a biguanide, poly(oxyethylene-(dimethylimino)ethylene(dimethylimino) ethylenedichloride), isothiazolinone, and quaternary ammonium compounds. In preferred embodiments the bactericide is triclosan or polyhexamethylene biguanide.

[0019] The fungicide may be selected from the group consisting of tolyldiiodomethylsulfone, zinc 2-pyridinethiol-1-oxide, propiconazole, thiabendazole, and tebuconazole. A preferred fungicide is tolyldiiodomethylsulfone.

[0020] The leather goods are also soaked in an aqueous solution containing dyes and tanning agents as is usual in a tanning process. Suitable tanning agents include wattle, (wattle is a natural product from the Mimosaceae plant indigenous to Australia that is a soluble astringent complex phenolic), dicyanodiamide, and dyes. A typical synthetic tanning agent is a solution of a salt of a maleic acid styrene copolymer, which is used to improve the fullness and tightness of grain. This copolymer typically lowers the pH of the solution to a slightly acidic condition: approximately 6.4. The step of soaking the

goods in a solution of dyes and tanning agents (hereinafter tanning agent solution) can occur prior to or after the first soaking in an antimicrobial agent. In trials used to test the effectiveness of the invention the step of soaking in the tanning agent solution occurred prior to the first soaking in antimicrobial agent. The leather is then rinsed at least once.

**[0021]** Tanning processes also include a step where the leather goods are "fatliquored". Fatliquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost earlier in the tanning process. Fatliquoring is usually performed in a drum with agitation using an oil emulsion at temperatures of about 50 °C to about 66 °C for anywhere between 30 minutes to several hours. This step usually includes adding waterproofing agents to the "fat liquor". The fat liquor is then drained and the hide is rinsed with water. In some instances the fat liquor may include tanning agents.

**[0022]** It was surprisingly discovered during the development of the invention that the timing of the first soaking of the goods in the antimicrobial composition affects the take-up or the exhausting of the antimicrobial agents into the leather. The terms take-up and exhaustion are used here in a manner similar to their use in a dyeing context. In general these terms refer to the amount of the antimicrobial agent absorbed or drawn into the leather. In particular, it was discovered that the application of the first antimicrobial soaking either prior to or concurrent with the first soaking of the leather goods in fat liquors greatly enhances the uptake of the antimicrobial agents into the leather and thus improves the antimicrobial durability of the leather.

**[0023]** Following the rinsing of the initial fat liquor solution from the leather goods, additional soakings in tanning agent solutions and fat liquor solutions may be utilized. Any number of tanning agent soakings, antimicrobial agent soakings and fat liquor soakings may occur as long as the antimicrobial soakings occur prior to or concurrent with the fat liquor soakings. In particularly preferred embodiments the antimicrobial composition is applied concurrently with the fat liquors.

**[0024]** Regardless of whether the antimicrobial composition is applied prior to or concurrently with the fat liquor, the leather goods should be soaked in the antimicrobial composition for a time sufficient to exhaust an amount of antimicrobial agents sufficient to achieve a commercially acceptable level of efficacy. In preferred embodiments the leather goods are soaked for a time sufficient to exhaust about 1000 ppm of fungicide and about 1000 ppm of bactericide into the leather. This level of exhaustion can occur in one soaking or multiple soakings. At the end of the antimicrobial soaking step or steps the leather should have bactericide and fungicide dispersed substantially throughout the leather, including the interior portions of the leather.

**[0025]** After the fat liquor soakings the leather is finished in accordance with any of the known finishing procedures. After the leather is finished it may then be formed into any number of end products. Such products include but are not limited to clothing, shoes, boots, coats, baggage, clothing accessories, tents, outdoor equipment, and upholstery.

**[0026]** A general flow chart for the method according to the invention which includes process settings used during trials is set forth below.

1. Obtain hides and scour hides to remove fat using a solution of metal salts of acetic acid, carbonic acid, formic acid and sulfurous acid. Adjust the pH of the solution to around 7.0 with sodium bicarbonate. In trials the hides were scoured for about 30 minutes.
2. Drain and rinse with water at least once.
3. Add water and wetting agents. Let soak for about 10 minutes.
4. Add dyes and tanning agents and let soak for about 60 minutes at about 33 °C. In trials a quantity of maleic acid styrene copolymer, a tanning agent, was added which lowered the pH to about 6.4 during this soaking step.
5. Drain and rinse with water at about 55 °C at least once.
6. Add water and the fat liquor and the antimicrobial composition. Let the leather goods soak, preferably with agitation, for about 80 minutes at 55 °C. In trials the antimicrobial composition comprised about 2000 ppm triclosan based

upon weight of goods and about 2500 ppm tolyldiiodomethylsulfone based upon weight of goods.

7. Add formic acid to the solution. Formic acid is a pickling agent that causes many of the more basic metal salts to attach to the formic acid. In trials the soaking in formic acid lasted about 60 minutes and the pH at this stage was about 3.9.

8. The formic acid solution is drained.

9. Water is added with an alkaline free chromic oxide solution. The leather is allowed to soak for about 60 minutes at about 33 °C.

10. The leather is then drained and rinsed with water at least once, preferably two or three times.

11. The leather is finished and formed into various end products.

**[0027]** More specific examples follow.

Example 1

**[0028]** A leather hide containing 1100 ppm of chloro-2(2,4-dichlorophenoxy)phenol and 1000 ppm of tolyldiiodomethylsulfone was prepared as follows.

**[0029]** The blue hide leather is washed in water and then scoured in an aqueous solution of sodium sulfite (2% on weight of good "owg"), sodium acetate (1.75% owg), sodium formate (1.75% owg), and sodium bicarbonate (0.75% owg). To this is added a mixture of the sodium salt of oleoylsarcosine in water (0.30% owg), chloro-2-(2,4-dichlorophenoxy)phenol (o.11% owg) and tolyldiiodomethylsulfone (0.1% owg). After soaking for 30 minutes, a solution of a salt of a maleic acid styrene copolymer is added (2.0% owg) and the leather is soaked for another 30 minutes. Then approximately 4% owg of water proofing agent is added with an additional 45 minutes of soaking. The aqueous solution is drained off and then the hide is rinsed.

[0030] The hide is then soaked in an aqueous solution of water proofing agents for 45 minutes, drained and rinsed with fresh water. The leather isthen soaked in Wattle, dicyanodiamide and black dyes. To this mixture is added 0.25% of the sodium salt of oleoylsarcosine in water. The hide is soaked for 60 minutes, drained and rinsed with fresh water.

[0031] To the rinse is added a second addition of the antimicrobial composition, which is a mixture of 0.11% owg of chloro-2-(2,4-dichlorophenoxy)phenol and 0.10% owg of tolyldiiodomethylsulfone. The hide is soaked for 20 minutes, and then another round of water proofing agents is added. To this solution is added 3.5% owg of formic acid, a pickling agent. The pH reading is about 3.9. After approximately 100 minutes, the solution is drained off and fresh water is added.

[0032] To the fresh water is added a chromic oxide cure, Chromitan® FM, a trademark of BASF, a lightly masked, alkaline free, basic chromium sulfate having a chromic oxide content of about 24% and a basicity of 40%. The chromic oxide breaks up the emulsifier of the water proofing agents making them permanent.

[0033] The resulting leather was then tested in accordance AATCC Test Method 147-1993, which quantifies the bactericidal efficacy against *S. aureus* and *K. pneumoniae*, and AATCC Test Method 30-1993, Part III which quantifies the fungicidal efficacy against *Aspergillus niger*. Results are shown in Tables 1 and 2.

Example 1b

[0034] Samples from Example 1 were laundered with an Atlas Laundrometer based on AATCC Test Method 61-2A. The samples were tested for anti-fungal efficacy according to AATCC Test Method 30-1993. The results of this test are shown in Table 2.

Example 2

**[0035]** A leather hide containing 4000 ppm (0.40% owg) of chloro-2-(2,4-dichlorophenoxy)phenol and 2000 ppm (0.20% owg) of tolyldiiodomethylsulfone was prepared and tested following the general procedure outlined in Example 1. These hides were tested in accordance with AATCC Test Methods 147 and 30. The results are shown in Tables 1 and 2.

Example 3

**[0036]** A leather hide containing 2500 ppm of poly(oxyethylene-(dimethylimino)-ethylene(dimethylimino)ethylenedichloride) and 2000 ppm of zinc 2-pyridinethiol-1-oxide was prepared and tested following the general procedure outlined in Example 1. These hides were tested in accordance with AATCC Test Methods 147 and 30. The results are shown in Tables 1 and 2.

**[0037]** Duplicate samples were run under AATCC Test Method 30, Part III which is why the samples in Table 2 are listed as #1 and #2.

Table 1

Test Method: AATCC Test Method 147-193

| Sample | Organism | Growth Descriptor | Zone of Inhibition (mm) |
|---|---|---|---|
| Example 1 | *S. aureus* | 0 | 6 |
| Example 1 | *K. pneumoniae* | 0 | 8 |
| | | | |
| Example 2 | *S. aureus* | 0 | 5 |
| Example 2 | *K. pneumoniae* | 0 | 8 |
| | | | |
| Example 3 | *S. aureus* | 0 | 17 |
| Example 3 | *K. pneumoniae* | 0 | 17 |

Table 2

Test Method: AATCC Test Method 30-1993, Part III

| Sample | Organism | Growth Descriptor | Zone of Inhibition (mm) |
|---|---|---|---|
| Example 1 (#1) | *A. niger* | 0 | - |
| Example 1 (#2) | *A. niger* | 0 | - |
| | | | |
| Example 1b (#1) | *A. niger* | 0 | 9 |
| Example 1b (#2) | *A. niger* | 0 | 9 |
| | | | |
| Example 2 (#1) | *A. niger* | 0 | 1 |
| Example 2 (#2) | *A. niger* | 0 | - |
| | | | |
| Example 3 (#1) | *A. niger* | 0 | - |
| Example 3 (#2) | *A. niger* | 0 | - |

Interpretation of Results
0 = no growth
1 = microscopic growth (visible under microscope)
2 = macroscopic growth (visible to naked eye)

**[0038]** Additional testing was conducted to further test the antimicrobial efficacy of leathers produced according to the invention. Various leathers were tested in accordance with AATCC Test Method 30 Part III and Kirby Bauer protocols. The leathers were tested as initially treated and after five (5) washings. As the results show, in all instances acceptable efficacy was demonstrated. In fact, zones of inhibition were demonstrated with samples that had been washed five times.

Table 3

Test Method: AATCC Test Method 30 Part III
Sample: 1.5 inch x 1.5 inch square of leather

| Sample | Organism | Growth Descriptor | Zone of Inhibition (mm) |
|---|---|---|---|
| | | | |
| Leather #1 | *A. niger* | 0 | - |
| Leather #1 | *T. mentagrophytes* | 0 | 18 |
| | | | |
| Leather #2 | *A. niger* | 0 | 5 |
| Leather #2 | *T. mentagrophytes* | 0 | 8 |
| | | | |
| Leather #3 | *A. niger* | 0 | - |
| Leather #3 | *T. mentagrophytes* | 0 | 16 |
| | | | |
| Leather #4 | *A. niger* | 0 | - |
| Leather #4 | *T. mentagrophytes* | 0 | 14 |
| | | | |
| Leather #5 | *A. niger* | 0 | 7 |
| Leather #5 | *T. mentagrophytes* | 0 | 13 |
| | | | |
| Leather #1 (wash 5x) | *A. niger* | 0 | - |
| Leather #1 (wash 5x) | *T. mentagrophytes* | 0 | 8 |
| | | | |
| Leather #2 (wash 5x) | *A. niger* | 0 | - |
| Leather #2 (wash 5x) | *T. mentagrophytes* | 0 | 11 |
| | | | |
| Leather #3 (wash 5x) | *A. niger* | 0 | - |
| Leather #3 (wash 5x) | *T. mentagrophytes* | 0 | 13 |

Interpretation of Results

0 = no growth
1 = microscopic growth (visible under microscope)
2 = macroscopic growth (visible to naked eye)

Table 4

Test Method: Kirby Bauer
Sample: 1 inch x 1 inch square of leather

| Sample | Organism | Results | Zone of Inhibition (mm) |
|---|---|---|---|
| | | | |
| Leather #1 | *E. coli* | NZ/I | - |
| Leather #1 | *S. aureus* | I | 3 |
| | | | |
| Leather #2 | *E. coli* | NZ/I | - |
| Leather #2 | *S. aureus* | I | 4 |
| | | | |
| Leather #3 | *E. coli* | NZ/I | - |
| Leather #3 | *S. aureus* | I | 3 |
| | | | |
| Leather #4 | *E. coli* | I | 6 |
| Leather #4 | *S. aureus* | I | 8 |
| | | | |
| Leather #5 | *E. coli* | I | 3 |
| Leather #5 | *S. aureus* | I | 6 |
| | | | |
| Leather #6 | *E. coli* | NZ/I | - |
| Leather #6 | *S. aureus* | I | 3 |
| | | | |
| Leather #1 (wash 5x) | *E. coli* | NZ/I | - |
| Leather #1 (wash 5x) | *S. aureus* | I | 1 |
| | | | |
| Leather #2 (wash 5x) | *E. coli* | NZ/I | - |
| Leather #2 (wash 5x) | *S. aureus* | I | 1 |
| | | | |
| Leather #3 (wash 5x) | *E. coli* | NZ/I | - |
| Leather #3 (wash 5x) | *S. aureus* | NZ/I | - |
| | | | |
| Leather #4 (wash 5x) | *E. coli* | I | 5 |
| Leather #4 (wash 5x) | *S. aureus* | I | 8 |
| | | | |
| Leather #5 (wash 5x) | *E. coli* | NZ/I | - |
| Leather #5 (wash 5x) | *S. aureus* | I | 4 |
| | | | |
| Leather #6 (wash 5x) | *E. coli* | NZ/I | - |
| Leather #6 (wash 5x) | *S. aureus* | I | 1 |

Interpretation of Results

I = Inhibition of growth
NZ = No zone of inhibition surrounding the sample
NZ/I = No zone of inhibition but growth was inhibited
NI = No inhibition of growth under the sample (if observable)

**[0039]** In view of the above, the invention also encompasses leather having durable antimicrobial properties. The leather according to the invention comprises an organic bactericide and a fungicide wherein the fungicide and bactericide are present in the leather in a ratio between about 1:50 to about 10:1 fungicide to bactericide. In preferred embodiments the fungicide is present between about 200 ppm and about 5,000 ppm based upon the weight of goods and the bactericide is present between about 500 ppm and 10,000 ppm based on the weight of goods. In particularly preferred embodiments the leather according to the invention contains at least 1000 ppm of fungicide and at least 1000 ppm bactericide. The fungicides and bactericides utilized and preferred in this embodiment are the same as those discussed with respect to the method.

**[0040]** The phrase "present in the leather" as used in this context means that the bactericide and fungicide are incorporated into the interior of the leather rather than just forming a coating on the surface of the leather or the outermost layers of the leather. An alternative description for the leather according to the invention would be that the antimicrobial agents are exhausted or fixed into the leather matrix which helps retain the agents and therefore provides the durability discussed above.

**[0041]** Finally, the invention also encompasses a composition utilized for the aqueous or in-situ treatment of leather in accordance with the invention; specifically an antimicrobial composition for in-situ treatment of leather comprising a bactericide and a fungicide wherein the fungicide and bactericide are present in the composition in a ratio of between about 1:50 to about 10:1 fungicide to bactericide. In preferred embodiments the fungicide is present in the composition between about 200 ppm and about 5,000 ppm and the bactericide is present in the composition between about 500 ppm and about 10,000 ppm based on the weight of the goods treated. The preferred bactericides and fungicides and combinations thereof are the same as those discussed in relation to the method according to the invention.